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Sodium-23 NMR and Complex Impedance Studies of Gel Electrolytes Based on Poly(acrylonitrile)

by

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Sodium-23 NMR and Complex Impedance Studies of Gel Electrolytes Based on Poly(acrylonitrile)

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ABSTRACT

Highly conducting gel electrolytes prepared from mixtures of poly(acrylonitrile) (PAN), ethylene carbonate (EC), propylene carbonate (PC) and $NaClO_4$ have been studied by complex impedance, differential scanning calorimetry (DSC) and ^{23}Na nuclear magnetic resonance (NMR) spectroscopy. Ionic motional correlation times spanning nearly five orders of magnitude, probed by temperature-dependent dynamical features of the ^{23}Na quadrupole-broadened NMR lineshape, are strongly influenced by the single glass transition temperature observed in the gel electrolyte. Dielectric measurements of mixtures of PAN, EC and PC suggest that the polar nitrile group in PAN may interact with Na^+ ions in the gel. All results are consistent with the conclusion that PAN provides stability to the gel network down to the immediate vicinity of the Na^+ ions, rather than acting as a rigid framework for regions of liquid electrolyte.

Introduction

Gel electrolytes formed by immobilizing liquid electrolytes in a rigid polymeric matrix offer a highly conducting alternative to solvent-free polyether-based electrolytes. Typical liquid electrolytes for lithium battery applications are lithium salts dissolved in propylene carbonate (PC) or a mixture of PC and ethylene carbonate (EC). Some of the matrix polymers employed in gel preparation have been poly(acrylonitrile) (PAN) [1-3] or poly(methylmethacrylate) (PMMA) [4,5]. The ion transport mechanism in these composite materials appears to be dominated by the liquid electrolyte, based on the observation that the conductivity of the gel is not much lower than that of the liquid electrolyte constituent. However, recent evidence suggests that the host polymer can also interact with the ions, especially for compositions having reduced EC/PC content. These interactions have been inferred from composition-dependent studies of macroscopic ionic conductivity and viscosity parameters [5]. In order to obtain more direct information concerning the presence of ion-polymer interactions it is necessary to employ microscopic techniques such as nuclear magnetic resonance (NMR), as was recently reported for PAN-based gels [6].

Physical characterization of electrolyte solutions and gels containing sodium salts is important due to the technological interest for applications such as sodium batteries [7]. ^{23}Na NMR has been successfully employed as a probe of ion-ion and ion-polymer interaction in polyether-salt polymer electrolytes [8]. The ^{23}Na nucleus (I=3/2) has a large electric quadrupole moment which makes it extremely sensitive to nearest neighbor coordination and thus a useful probe of both structure and dynamics. We have performed complex impedance, NMR and differential scanning calorimetry (DSC) measurements on gel electrolytes containing $NaClO_4$

and on corresponding liquid electrolytes, in order to test the hypothesis that the conductivity mechanism in the gel is the same as that in the liquid.

Experimental

Gel electrolytes were prepared from high purity PC (Burdick & Jackson), EC (Fluka), PAN (Polyscience, average molecular mass 1.5 X 10^5 grams/mole) and $NaClO_4$ (Aldrich 99+ %). Further purification of the solvents and PAN are described in an earlier publication [6]. $NaClO_4$ was recrystallized from a water:acetone (1:5) mixture and dried in vacuum at 180°C for at least 12 hours. Two compositions were studied: $PAN_{21}EC_{38}PC_{33}(NaClO_4)_8$, with an EC/PC : Na ratio of nearly 9:1 and $PAN_{21}EC_{40}PC_{34.75}(NaClO_4)_{4.25}$, with an EC/PC : Na ratio of almost 18:1. Hereafter, the samples will be referred to as sample A and sample B for the higher and lower salt concentrations, respectively. For comparison two liquid electrolytes were also prepared, with EC/PC : Na of 9:1 and 18:1. The first liquid is 1.7 M $NaClO_4$ in a 1:1 (molar) mixture of EC and PC; the latter solution containing half as much salt (0.85M). All sample manipulations were performed under drybox conditions.

DSC measurements were performed on a Mettler TA3000 Thermal Analysis System. Electrical conductivities were determined from ac impedance measurements utilizing an EG&G PAR model 398 impedance system with #316 stainless steel blocking electrodes. Dielectric constants and, in some cases, the dissipation factor (*tan* δ) were determined at room temperature (297 $\pm$ 1 K) from capacitance measurements using a HP4284A Precision LCR Bridge and a HP 16048C test fixture. Measurements were made from 20 Hz to 1 MHz using an ac signal of 10 mV amplitude. All dielectric constants reported are those for 1 MHz

at which frequency the dissipation factors are small and the dielectric contant, ε is independent of frequency. For the pure liquid having an EC/PC mole ratio of 1.151, a "dip-type" cell was utilized: i.e. a vertical three-terminal guarded concentric electrode assembly attached to the bridge with a General Radio 0874 connector. The dielectric cell was calibrated in air after short and open circuit corrections were made. For gel samples (mixtures of PAN and EC/PC), two stainless steel blocking electrodes separated with a Teflon spacer served as the dielectric cell. A mercury cell of 1.905 cm diameter was utilized for measuring the dielectric constant of pure PAN. The dielectric constants were calculated from the experimental capacities, C, from the standard relation $C = \varepsilon_o \varepsilon A/t$, where ε_o is the free space permittivity constant and A and t are the electrode area and spacing, respectively.

NMR measurements were performed at 81.5 MHz on a Novex broadband spectometer and also a Chemagnetics CMX 300 spectrometer. For a sample volume of ~ 0.7 cm^3, good signal-to-noise was obtained with 24 - 200 transients, the higher numbers necessary for low temperature broad spectra. Spin-lattice relaxation times (T_1) values were extracted from recovery profiles of the inversion recovery pulse sequence. Low temperature recoveries (below T_g) were non-exponential; which reflects the broad distribution of relaxation times.

Results

The DSC results are quite similar to those reported previously for identical gel compositions prepared with $LiClO_4$ [6]. DSC thermograms for the two gels are shown in Fig.1. The gels are homogeneous amorphous materials as evidenced by the single strong glass transition occurring at 183K and 195K in samples B and A,

respectively. As in the case of the Li gel electrolytes, the differences in T_g are attributed to the different salt concentrations and perhaps partly to the slightly lower PAN : EC/PC ratio in the material with the lower salt concentration (and lower T_g).

Electrical conductivity data for the two gels and reference liquid electrolyte consisting of 0.85 M $NaClO_4$ in a 1:1 mixture of EC/PC are shown in Arrhenius plots in Fig.2. The ionic conductivities of the two gels are approximately equal and not much lower than that of the liquid, in the range 295 - 325K. Below 295K, sample B exhibits higher conductivity even though it has a lower salt, and presumably lower carrier, concentration than sample A. As in the case of polyether-based electrolytes, microviscosity of the conducting medium affects conductivity more than carrier concentration (above a critical concentration) [9]. Fig. 3 shows that the ionic conductivity of sample B is higher than that of a similar composition gel made with $LiClO_4$, but somewhat lower than that of a gel containing $LiAsF_6$. The conductivity temperature dependence follows a VTF relationship [10], given by

$$\sigma = AT^{-1/2}\exp[-E_a/k(T-T_o)]. \qquad (1)$$

The solid lines in Fig.2 are plotted from the best fit VTF parameters, listed in Table 1.

In a previous study on lithium gel electrolytes it was suggested that the PAN chains can be more than just passive components of the gel. That is, in addition to providing dimensional stability they may also interact with the ions [6]. Additional evidence for this is presented in Fig.4, which is a plot of dielectric constant vs. PAN concentration in mixtures of EC/PC (again in a 1.15 ratio) and

PAN. The dielectric data in Fig.4 is also listed in Table 2. We chose to measure the dielectric properties of the gel components minus the salt because the high conductivity of the electrolyte prevents determination of the dielectric constant at audio frequencies. The dielectric constant is, of course, closely related to the solvating ability of the medium. The dielectric constant of pure PAN has been reported as 6.5 at 298K [1], whereas our measurements yield a value of 4.3. However it is noted that the PAN used in Ref. [1] had an average molecular mass of 9.4 X 10^4 and that ε was measured at a frequency of 60 Hz. Our results for pure PAN show that at low frequencies, the dielectric loss is small but still significant; i.e. at 100 Hz we obtain a value of tan $\delta = 0.043$ and $\varepsilon = 5.8$ which decreases to tan $\delta = 0.012$ and a constant value of $\varepsilon = 4.3$ at 1 MHz. Our value for the pure liquid (EC/PC) is 76.7 which is in good agreement with the interpolated value of 78.4 from the data of Seward and Viera [11]. The straight line in Fig. 4 represents the value of the dielectric constant predicted from a weighted average of the constituents, assuming a value of 76.7 for EC/PC = 1.15 and 4.3 for pure PAN. The data points show significant enhancement above the predicted values. Therefore the value of 4.3 for PAN, well below its glass transition temperature, is not relevant for PAN in the highly plasticized state which characterizes the gels. It is also clear that a single effective value of enhanced dielectric constant for PAN does not adequately explain the data because the experimental points would then be expected to intersect the theoretical line in the limit of x (PAN mole fraction) = 0. However, details concerning the compositional dependence of the effective dielectric constant of PAN are beyond the scope ot this investigation. Even though the cations may be solvated in large part by EC or PC (since compositionally PAN has a lower molar content than EC/PC), it is reasonable, on the basis of this result, to suggest that polar PAN

segments in the gel can compete with EC and PC for Li^+ or Na^+ solvation. The enhancement in dielectric constant is, admittedly, a crude and indirect probe of solvation properties, but the purpose here is to indicate plausibility of the PAN - ion interaction. Specific analysis of the solvation shell would require direct spectroscopic results such as vibrational frequency shifts in gels with and without salts, or perhaps double resonance NMR involving the ion and the nitrile group (i.e. ^{13}C - ^{23}Na or ^{14}N - ^{23}Na).

The low temperature ^{23}Na NMR spectra indicate a disordered heterogeneous environment for the Na^+ ions. Similar conclusions regarding the heterogeneous environment of Li^+ ions were drawn from low temperature ^7Li lineshapes in PAN-$LiClO_4$ gels [6]. Representative ^{23}Na spectra for sample A are shown in Fig. 5; where the lineshape changes significantly with temperature. Generally, lineshapes are symmetric and single peaked. Lineshape asymmetry due to chemical shift anisotropy was either absent or could not be resolved due to distributions in the sodium ion environment. All ^{23}Na transitions are observed in NMR responses above 223K. The dramatic reduction in the $\pi/2$ pulse width as the temperature was lowered below 223K (8μsec to 4μsec) supports the conclusion that only the central $+1/2 \leftrightarrow -1/2$ transition could be resolved in the low temperature responses [12]. The temperature dependent linewidths follow the trend expected for a spin 3/2 nucleus in the presence of electric quadrupolar interactions [8] and are shown for gel samples A and B in Fig. 6.

Between 253 and 333K the linewidth of sample A decreases with increasing temperature. The ^{23}Na lineshape in this temperature regime is characterized by the line-narrowing effect of large scale ionic motions upon potential line-broadening mechanisms (magnetic dipole-dipole, chemical shift anisotropy and electric quadrupole interactions). Near 253K the linewidth values achieve a local

maximum indicative of motional correlation times on the order of $(\omega_L)^{-1}$; i.e. inverse Larmor frequency (10^{-9} - 10^{-8} sec).

As the temperature is lowered from 253K to about 223K the linewidths decrease. This behavior arises due to hindered ionic motions characterized by correlation times on the order of $(\omega_Q)^{-1}$ (10^{-6} sec); which is the inverse of a motionally averaged electric quadrupole frequency. Fig. 5 shows some typical NMR responses from the gel (sample A). In particular, note the broadening for the line at 263K; which arises due to the effect of 1st-order quadrupole interactions on the satellite $\pm(3/2 \leftrightarrow 1/2)$ transitions. Due to the distributions of sodium ion environments; the divergent features of the satellite response are smeared. Additionally, the breadth of the satellite response is temperature dependent, and reflects the degree to which the 1st-order quadrupole interaction is motionally averaged.

For temperatures lower than 223K the linewidth again increases then levels off at the rigid limit, corresponding to the glass transition. The onset of the rigid linewidth values occurs when the correlation time is on the order of $\omega_L/(\omega_Q)^2$ (10^{-5} - 10^{-4} sec). From the rigid linewidth (between 3.0 and 3.5 kHz), the strength of the quadrupole interaction $\omega_Q/2\pi$ can be estimated to be on the order of 1 MHz [13]. This estimate includes the assumption of 2nd-order quadrupole broadening at low temperatures (as previously mentioned only the central transition is observed for temperatures below T_g); which was verified by the increase in ^{23}Na linewidth observed for measurements performed at 51 MHz.

The behavior of sample B is nearly identical to that of A, except that all of the features are shifted to lower temperature by about 10K. This temperature difference is also accompanied by a similar difference in T_g between the samples. Linewidths of the reference liquid electrolytes are plotted in Fig. 7. The behavior

of the liquid electrolyte linewidths is similar to that of the gels, including a temperature shift of about 15K between the higher and lower salt concentrations. The dynamic features are shifted to lower temperatures by about 25 to 30K in the liquids relative to the gels.

Additional dynamical information is available from T_1 data. Arrhenius plots of T_1 of the gels and liquids are displayed in Figs. 8 and 9, respectively. Recovery profiles yield T_1 values accurate to within 10% and appear to be exponential for temperatures down to T_g. T_1 values gathered for temperatures below T_g (subject to at least 25% error) were estimated using the best exponential fit to the data. However, it should be emphasized that spin-lattice recovery behavior is non-exponential below T_g; and in our view, is reflective of a large distribution of T_1 values characterizing a disordered heterogeneous sodium ion environment.

In the gels, clear T_1 minima are observed, at ~ 233K and ~223 K for samples A and B, respectively. Because the T_1 minimum also signifies a correlation time of ~ $(\omega_L)^{-1}$, it is apparent that the linewidth maxima in Fig.6 do not exactly correspond to the T_1 minima, but are shifted to higher temperatures by about 15 - 20K. This temperature offset between the linewidth maximum and the T_1 minimum has been observed previously in polymer electrolytes [13], and is attributed to the presence of other line broadening mechanisms in addition to the quadrupole interaction (i.e. ^{23}Na - ^{1}H dipole-dipole; chemical shift anisotropy, etc.). The liquid electrolytes also exhibit clear T_1 minima, occurring at ~ 218K and 203K in the larger and smaller salt concentrations, respectively. It is interesting that for the previously cited investigation of PAN gels containing $LiClO_4$, the gels showed a large shift in the ^{7}Li T_1 minimum, as a function of salt concentration, while the corresponding reference liquids did not [6].

From the Arrhenius plots in Figs.8 and 9, simple linear fits to the data on the high temperature side of the T_1 minima can be utilized to extract activation energies for ^{23}Na relaxation; the results are listed in Table 1. The activation energies of the gels are similar to each other and about 30% smaller than those of the liquids. This is opposite to the result that would be expected on the basis of the conductivity results. That is, straight-line (Arrhenius) fits of the conductivity data over the same temperature range as the T_1 fits would yield slightly higher activation energies for the gels relative to the liquids. However it is important to realize that T_1 probes motions on the timescale of $(\omega_L)^{-1}$ which are, at best, only indirectly related to ionic conductivity.

Discussion

In a previous study of PAN-based gel electrolytes containing lithium salts, it was established that the onset of ionic mobility was correlated with the glass transition of the gel [6]. The same conclusion must be drawn from the results of this investigation of the sodium-containing gels. Furthermore, owing to the dynamic range of ionic correlation times probed by the ^{23}Na quadrupole interaction, it is observed that correlation times spanning nearly 5 orders of magnitude are all shifted by changes in T_g, which in turn, depends on salt concentration. Although T_g's of the reference liquid electrolytes were not measured (nor was it determined that there might be a crystalline phase at low temperature), shifts in ionic correlation times with salt concentration of the liquids are also observed.

As mentioned previously, the dielectric results suggest that the cations could

be partially solvated by PAN, even though the high EC/PC:PAN ratio of the gels implies that the cations are mostly solvated by EC/PC, as in the liquid electrolyte. The NMR results demonstrate that the PAN is not a rigid, non-interacting matrix in which small regions of liquid electrolyte can reside, but rather part of an amorphous network that constitutes the gel. Above its glass transition temperature, this network determines the nature of the Na^+ dynamics down to the shortest timescale probed by NMR ($\sim 10^{-9}$sec), thus ruling out even microscopically small regions of "pure" liquid electrolyte.

Recent infrared polarization studies of salt-free gels formed from mixtures of PAN and EC or gamma butyrolactone (γBL) suggest pairing of the EC or γBL molecules with nitrile groups on the PAN chain [14]. This result is consistent with the dielectric results reported here, in that the highly polar nitrile group is regarded as a gel constituent rather than part of a rigid matrix polymer. The results reported here support the concept that the gel components are completely miscible (i.e., the presence of salt in the gel electrolytes does not eliminate the interaction between PAN and EC/PC). Moreover, the gel can be envisioned as a continuous network of PAN and EC/PC down to the immediate vicinity of the Na^+ ions. Below T_g, there appears to be no single preferred structural environment for Na^+; which can at best be described as heterogeneous and reflects large variations in the manner in which Na^+ ions are solvated by the gel.

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Figure Captions

Figure 1. DSC Thermograms for (A) $PAN_{21}EC_{38}PC_{33}(NaClO_4)_8$, and (B) $PAN_{21}EC_{40}PC_{34.75}(NaClO_4)_{4.25}$. The scan rate is 10K/minute.

Figure 2. Arrhenius plots of electrical conductivity for gel electrolytes and for 0.85 M $NaClO_4$ in 1:1 mixture of EC/PC.

Figure 3. Arrhenius plots of electrical conductivity for gel electrolytes containing $NaClO_4$, $LiClO_4$ and $LiAsF_6$.

Figure 4. Dielectric constant of $PAN_{1-x}(EC/PC)_x$ as a function of x. Data from Table 2 is plotted, where the straight line is the dielectric behavior from a weighted average of the endpoint values (x = 0 and x = 1).

Figure 5. ^{23}Na NMR spectra (81.5 MHz) of $PAN_{21}EC_{38}PC_{33}(NaClO_4)_8$ at 333, 263, 223 and 163K.

Figure 6. ^{23}Na NMR linewidths versus inverse temperature of the gel electrolytes; 9:1 gel (sample A = solid circles), 18:1 gel (sample B = open circles).

Figure 7. ^{23}Na NMR linewidths versus inverse temperature of reference liquid

electrolytes; (EC/PC):$NaClO_4$ = 9:1 (solid circles) and (EC/PC):$NaClO_4$ = 18:1 (open circles).

Figure 8. Arrhenius plots of ^{23}Na spin-lattice relaxation times (T_1) of the gel electrolytes; 9:1 gel (sample A = solid circles), 18:1 gel (sample B = open circles).

Figure 9. Arrhenius plots of ^{23}Na spin-lattice relaxation times (T_1) of reference liquid electrolytes; (EC/PC):$NaClO_4$ = 9:1 (solid circles) and (EC/PC):$NaClO_4$ = 18:1 (open circles).

Table 1

VTF parameters for ionic conductivity and Arrhenius activation energies for NMR T_1.

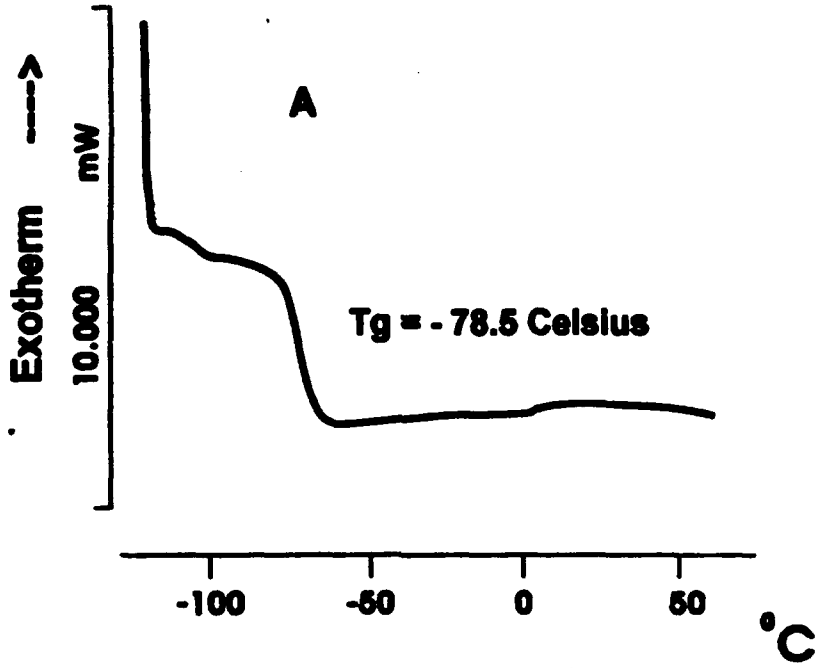
Electrolyte	(EC+PC):salt	A	T_0	Ea (eV) σ	Ea (eV) T_1
45EC:45PC:10$LiClO_4$	9:1	2.68	176	0.036	———
45EC:45PC:10$NaClO_4$	9:1	0.70	196	0.019	0.234
47.3EC:47.3PC:5.4$NaClO_4$	17.5:1	0.49	190	0.016	0.212
38EC:33PC:21PAN:8$LiClO_4$	8.8:1	13.9	162	0.068	0.13[a]
38EC:33PC:21PAN:8$NaClO_4$ (A)	8.8:1	3.38	179	0.054	0.145
40EC:34.75PC:21PAN:4.25$NaClO_4$ (B)	17.6:1	1.94	167	0.048	0.171

[a] E_a from T_1 data obtained from Ref. [6].

Table 2

Dielectric constants of EC:PC:PAN films measured at 1 MHz and 24°C. Molar ratio of EC/PC equal to 1.15.

Mole fraction (EC+PC)	ε
0	4.2
0.579	55.4
0.648	61.6
0.779	76.8
0.812	78.7
0.876	83.5
0.899	86.4
1	76.7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-100
-50
0
50
°C

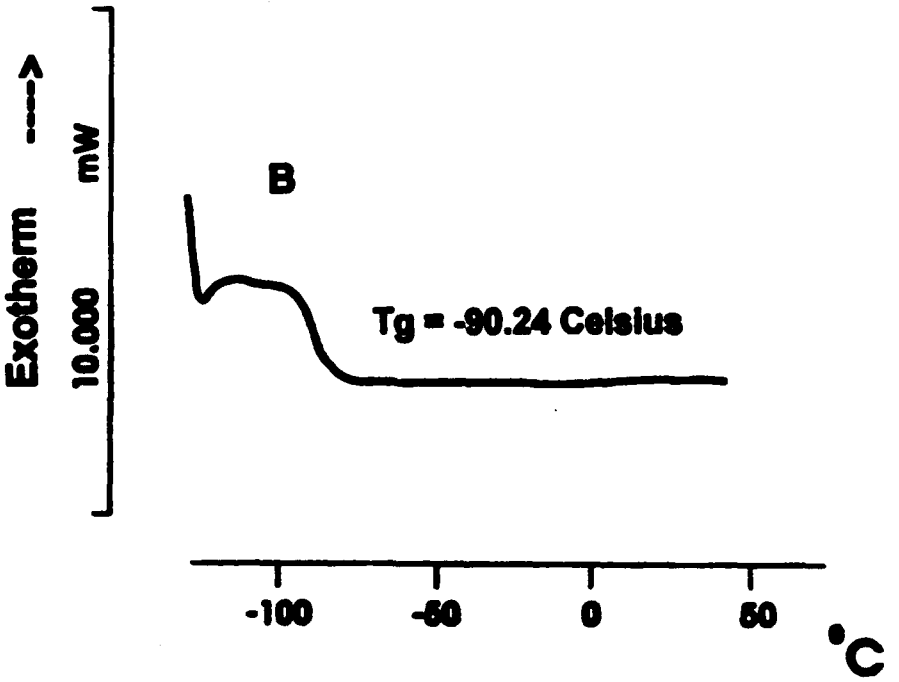

B
Exotherm ---> mW
10.000
Tg = -90.24 Celsius
-100
-50
0
50
°C

Fig 1

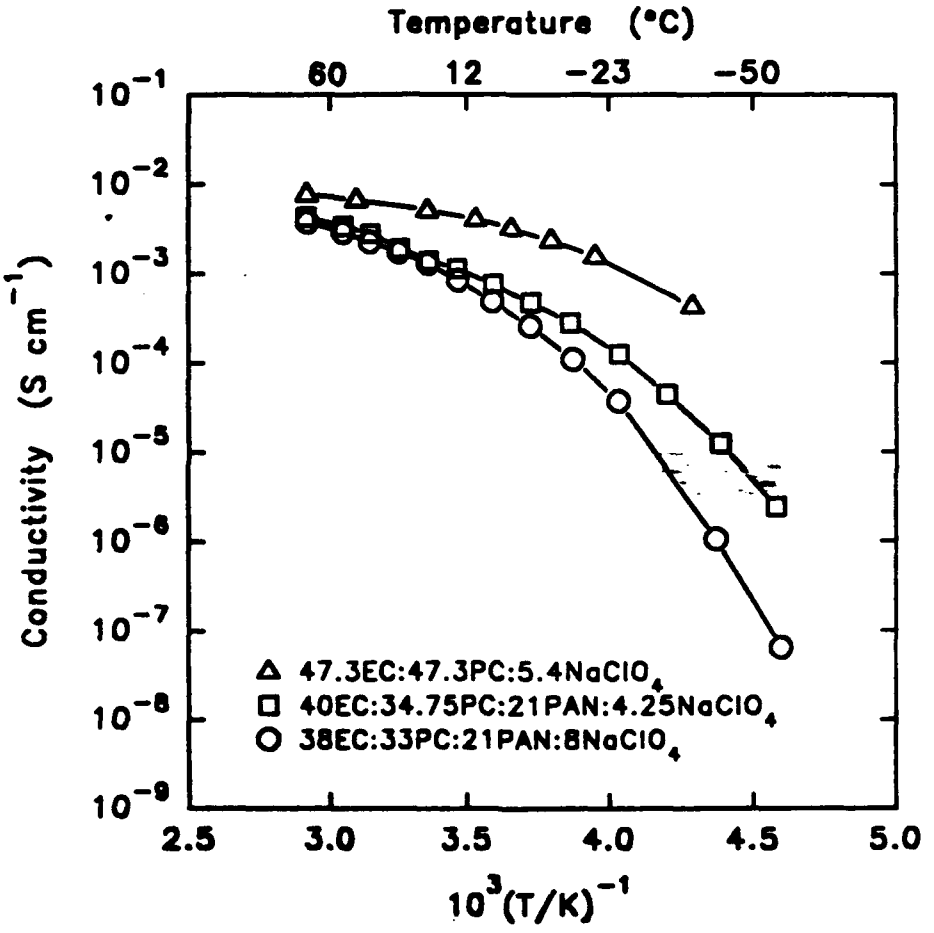

Temperature (°C)
60
12
−23
−50
Conductivity (S cm^{-1})
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
2.5
3.0
3.5
4.0
4.5
5.0
$10^3(T/K)^{-1}$
△ 47.3EC:47.3PC:5.4NaClO$_4$
□ 40EC:34.75PC:21PAN:4.25NaClO$_4$
○ 38EC:33PC:21PAN:8NaClO$_4$

Fig 2

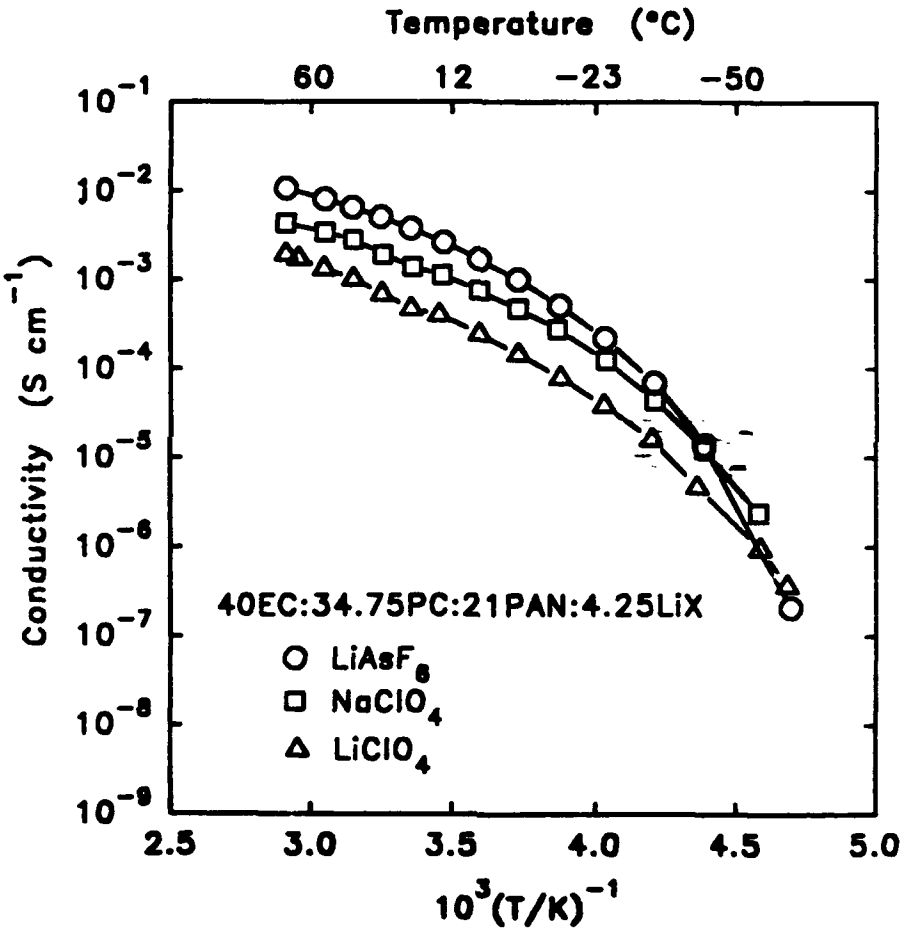
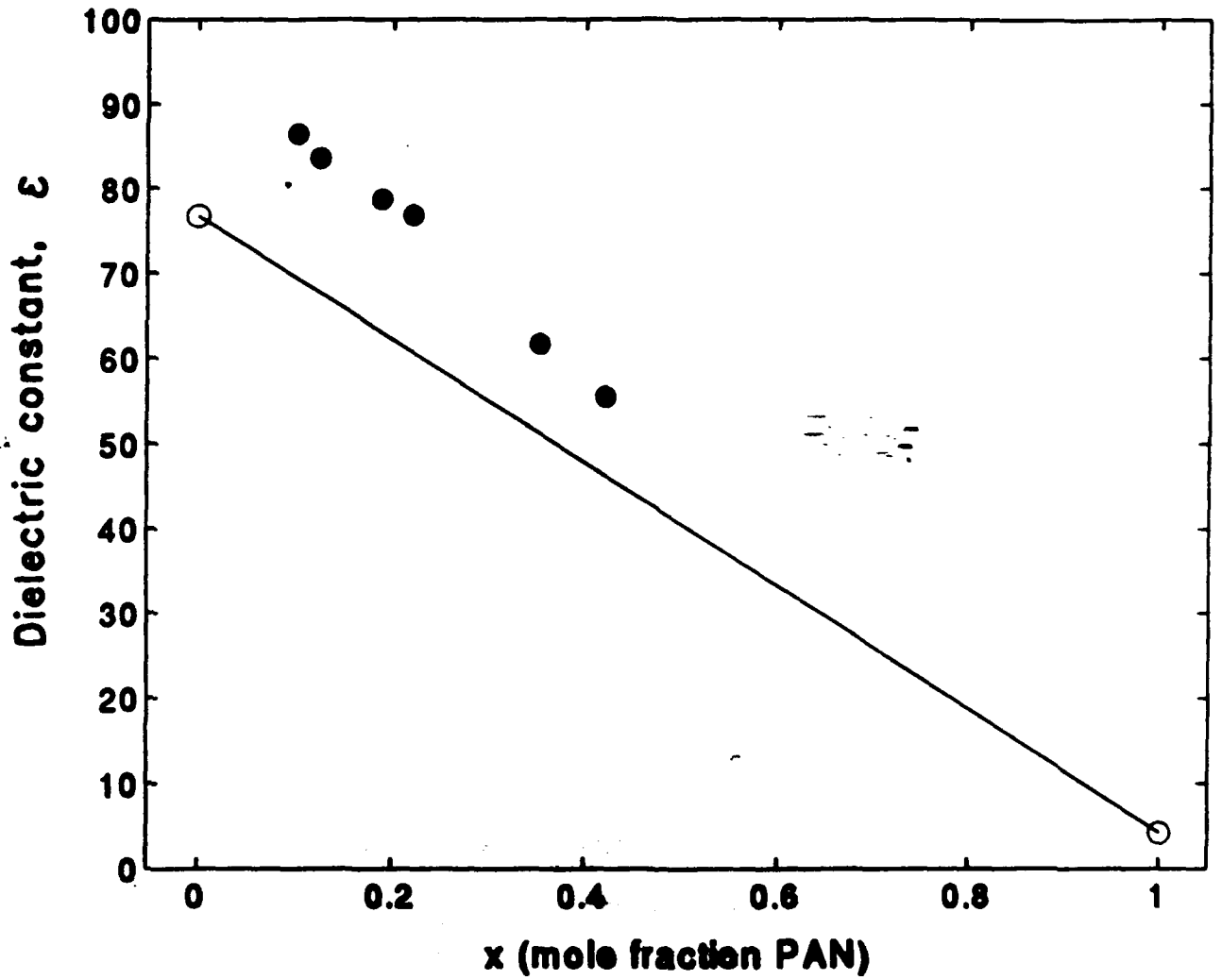

Temperature (°C)
60
12
−23
−50
Conductivity (S cm^{-1})
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
40EC:34.75PC:21PAN:4.25LiX
LiAsF$_6$
NaClO$_4$
LiClO$_4$
2.5
3.0
3.5
4.0
4.5
5.0
10^3(T/K)$^{-1}$

Fig 3


Dielectric constant, ε
100
90
80
70
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
x (mole fraction PAN)

Fig

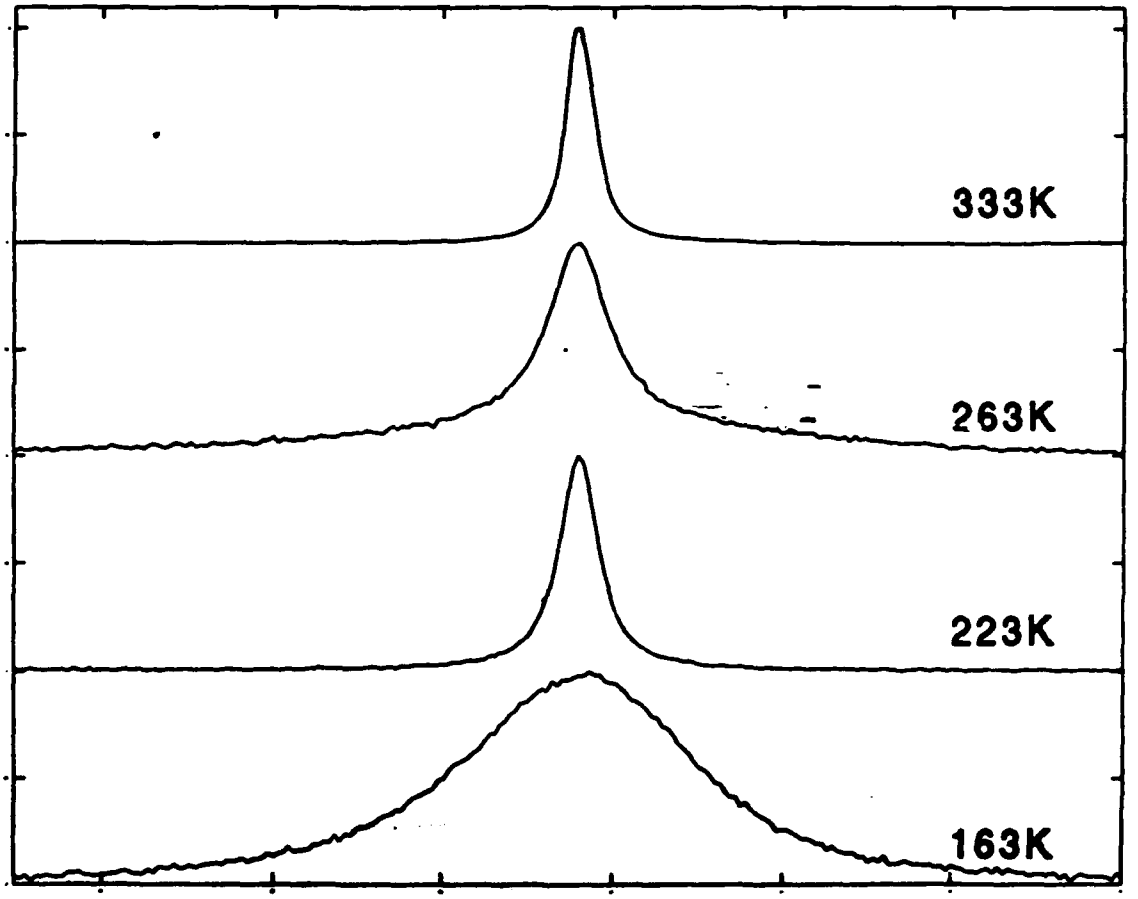


Fig 5

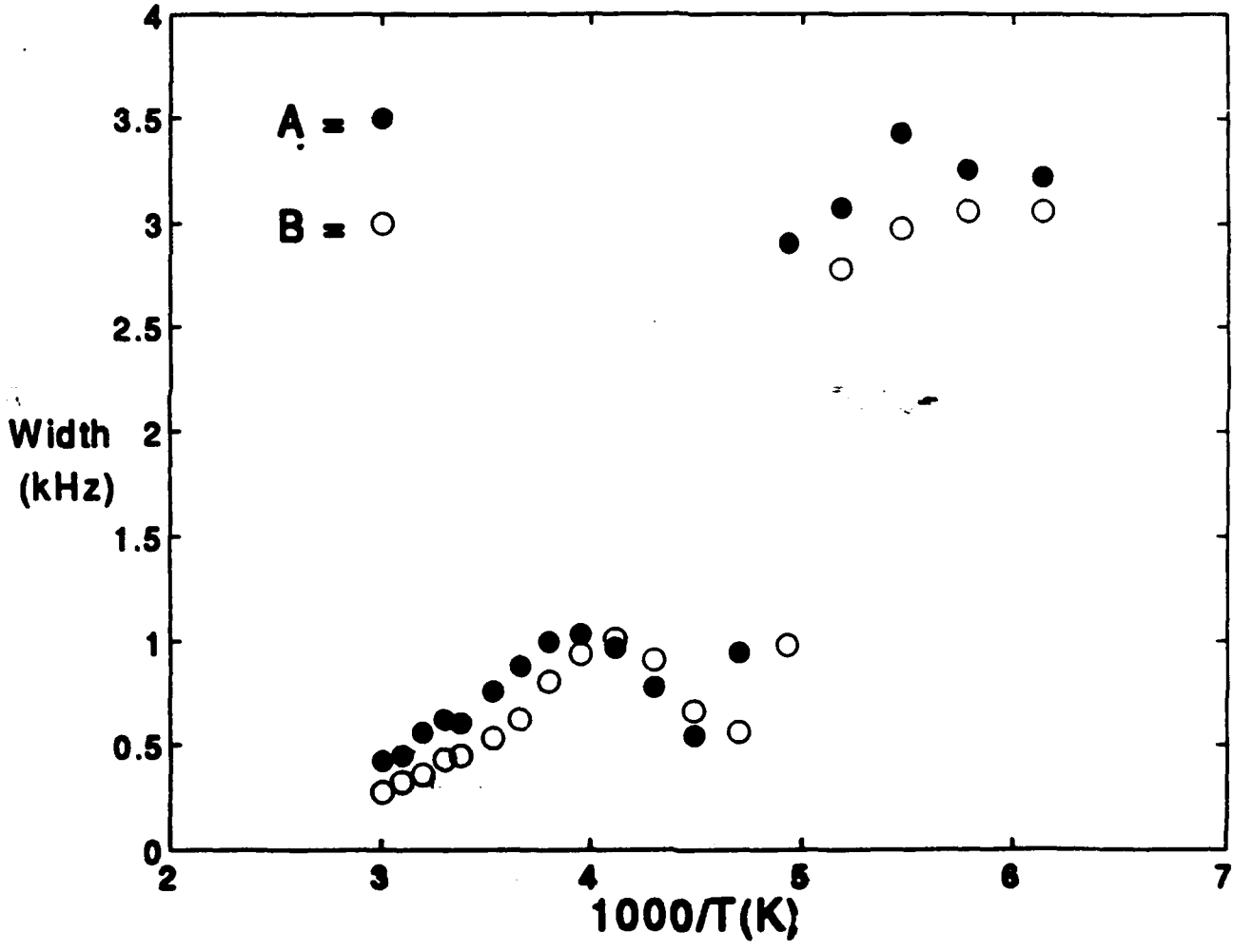


Fig 6

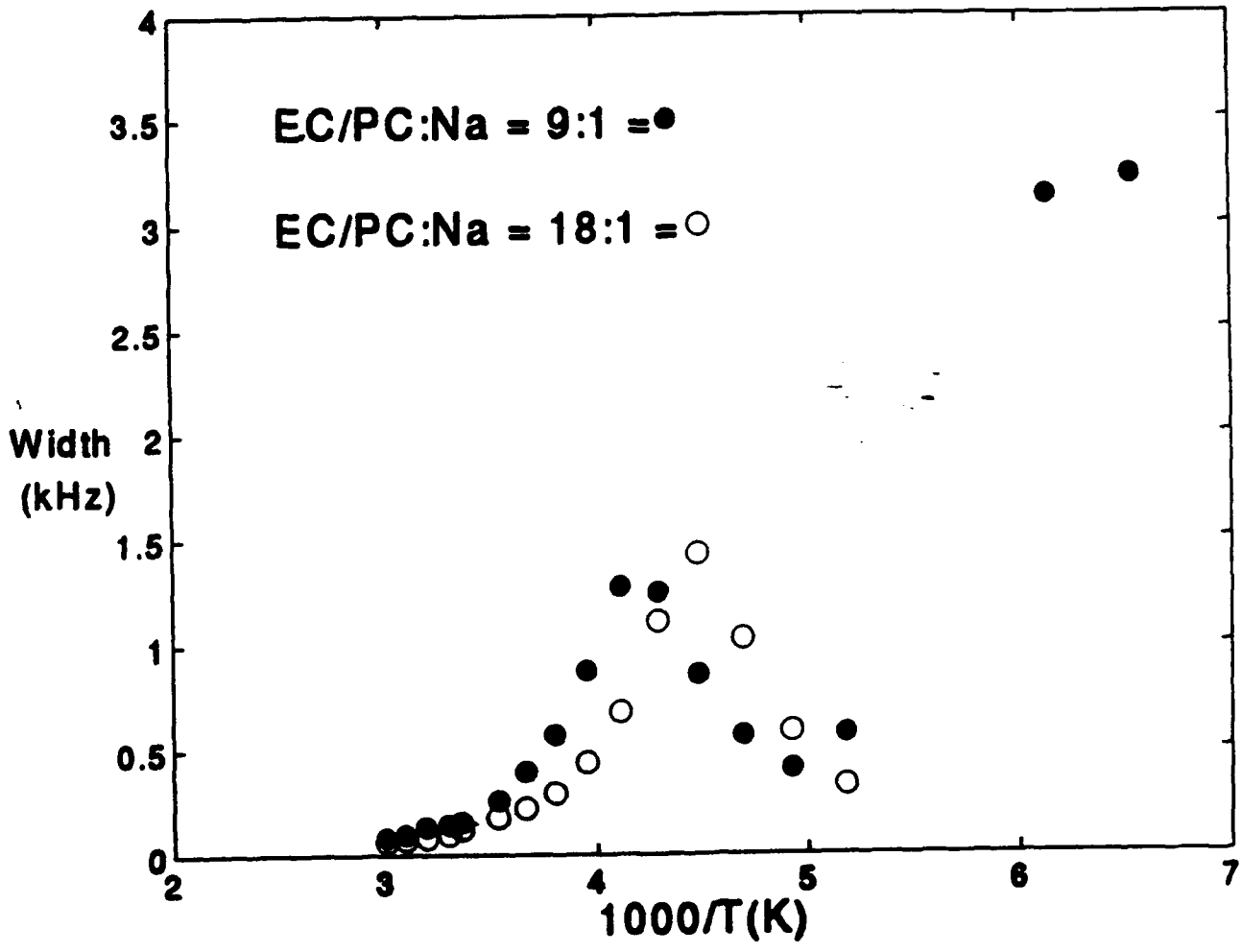

EC/PC:Na = 9:1 =●
EC/PC:Na = 18:1 =○
Width (kHz)
1000/T(K)
0
0.5
1
1.5
2
2.5
3
3.5
4
2
3
4
5
6
7

Fig 7

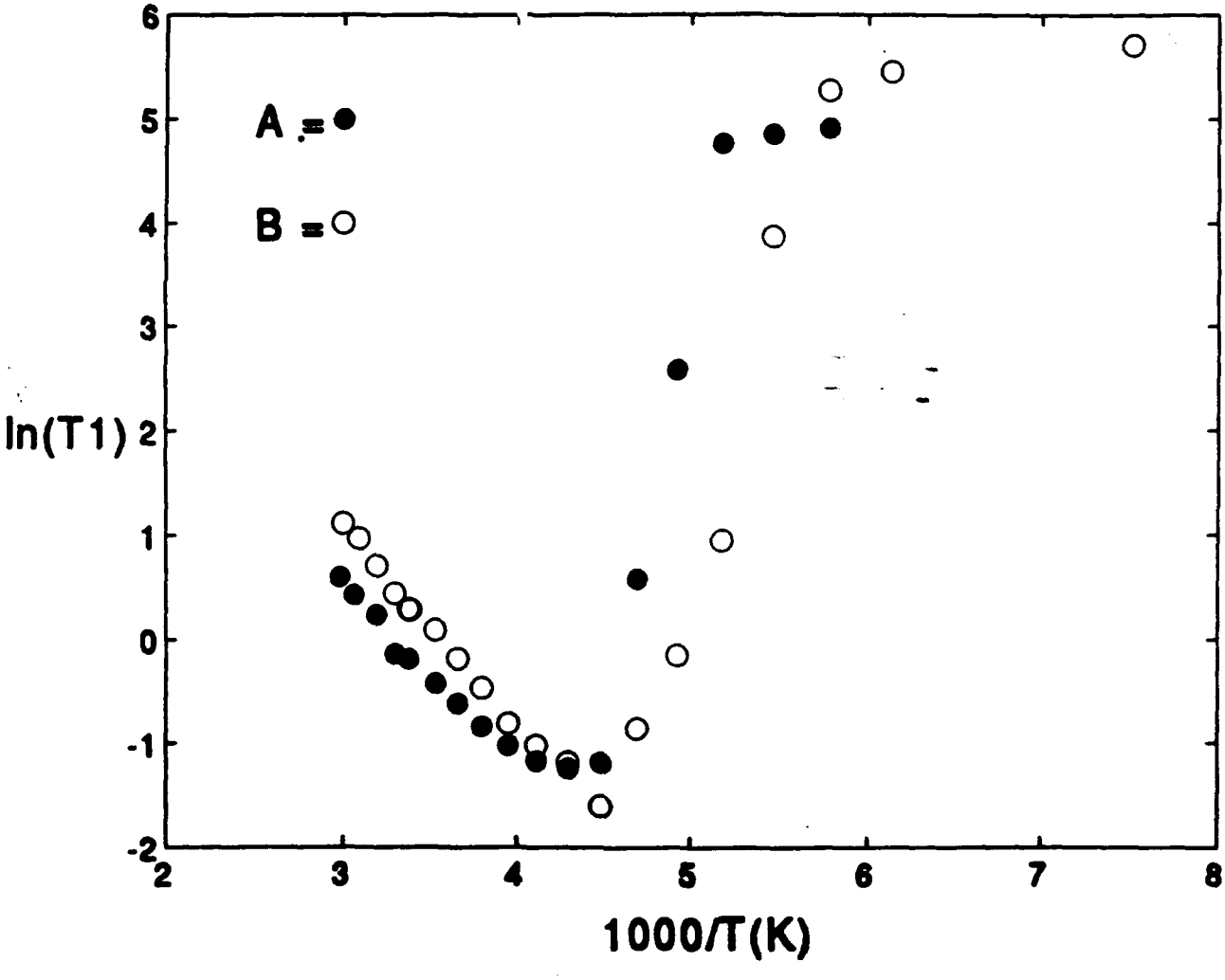


Fig 2

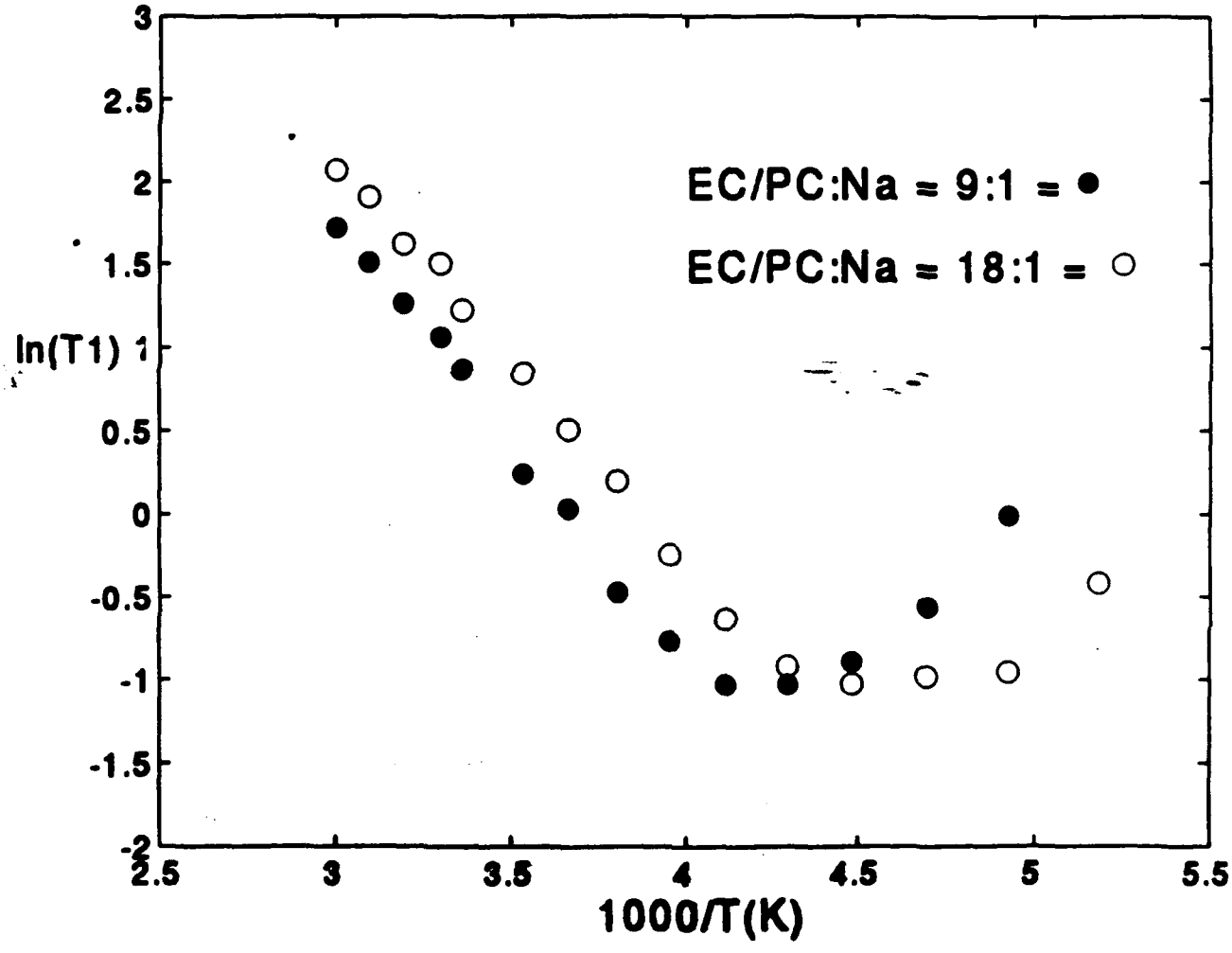

EC/PC:Na = 9:1 =
EC/PC:Na = 18:1 =
ln(T1)
1000/T(K)
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
2.5
3
3.5
4
4.5
5
5.5

Fig 9